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HENRY EYRING (1901–1981): A 20th CENTURY PHYSICAL CHEMIST AND HIS MODELS

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1. EYRING'S LECTURES

He would fill the blackboard with his equations.
He would begin in one corner;
he would describe his model with picturesque visualizations;
he would give the phenomenological equations;
he would develop his model drawing on statistical mechanics;
he would stop, charismatically introduce a needed supporting derivation;
he would carefully draw a chalk line around each supporting argument setting it aside from the main argument.

The blackboard took on the appearance of a patchwork quilt.

He would recognize that the equation just written made an incorrect physical statement;
he would back up and with self-effacing good humor analyze for the error then proceed;
he would go back and forth across the blackborard using every available square inch of space;
he would carefully draw lines separating each supporting derivation from the main derivation.

The patchwork quilt took on the quality of an intricate, elegant mosaic with a bold main theme and with many supporting background themes.

It was an exercise in logic;
it was an entertaining demonstration of rare insight;
it was a philosophical approach to new problems;
it was the tools for future research;
it was a description of the behavior of molecules;
it was understanding the physical process under development;
it was fundamental physical chemistry.

To the enraptured listener, it didn't matter how many times a lecture had been heard; for each time a new nuance became apparent, a greater depth of understanding achieved; more of his insight became apparent.

It was two-dimensional space, that blackboard, but it was always an N-dimensional virtuoso performance.

It was vintage Eyring.

2. EYRING'S ELEMENTARY FORMULATION OF STATISTICAL MECHANICS

Eyring commanded an unusual depth of understanding of the physics and chemistry of molecules and it was only natural that he would have his own elementary formulation of statistical mechanics [1–3] which provided him with the bridge between molecular descriptions and their macroscopically measurable equilibrium and, of course, dynamic properties. There are derivations of the fundamental equation of statistical mechanics, the Boltzmann law of energy distribution, which utilize idealized states, e.g., those represented by the perfect gas law. This can be done in the simple derivation of the barometric formula, i.e.,

$$P/P_0 = N/N_0 = \mathrm{e}^{-mgh/kT}, \tag{1}$$

where P and N are the pressure and number of molecules per unit volume in appropriate units at a given elevation, h, and P_0 and N_0 are for a reference state, e.g., at sea level with $h = 0$. The quantity mgh would then be the energy required to raise the molecules above sea level. Eyring would often use this simple approach in an introductory way comparing a cubic centimeter of air over the Rocky Mountains with one at sea level. He would then proceed to his general compounding of systems method. In the latter formulation [1–3], a system A (e.g., a benzene molecule of energy ϵ_i) in thermal equilibrium with a system B (e.g., a soft metal container comprised of s oscillators) was considered in terms of the number of ways, $N(n_i, s, \epsilon_i)$, that $n_i[= (E - \epsilon_i)/h\nu]$ quanta could be distributed among the s oscillators of system B, given a total energy E. Assuming the quanta to be indistinguishable (simply but importantly because this assumption gives agreement with experiment!) yields

$$N(n_i, s, \epsilon_i) = \frac{(n_i + s - 1)!}{(s-1)!n_i!}. \tag{2}$$

By appropriate cancellation of the common $n_i!$, by evaluating the remaining factorials in the numerator, by defining γ as the average energy of an oscillator, i.e., $\gamma = (E - \epsilon_i)/s$, and by requiring that $E \gg \epsilon_i$ and $n_i \gg s$ such that $\gamma \gg h\nu$, then

$$N(n_i, s, \epsilon_i) = C\,\mathrm{e}^{-\epsilon_i/\gamma}, \tag{3}$$

where

$$C = \frac{1}{(s-1)!}\left(\frac{\gamma s}{h\nu}\right)^{s-1} \tag{4}$$

If we now invoke the relevant fundamental assumption of theoretical thermodynamics, i.e., a statement of the ergodic hypothesis, that any unique, exactly specified way of distributing the quantized energy E in the combined system $A + B$ is equally probable, then the probability, P_i, that system A, for example, will have energy ϵ_i becomes

$$P_i = \frac{N(n_i, s, \epsilon_i)}{\sum_i N(n_i, s, \epsilon_i)} = \frac{C\,\mathrm{e}^{-\epsilon_i/\gamma}}{\sum_i C\,\mathrm{e}^{-\epsilon_i/\gamma}} = \frac{\mathrm{e}^{-\epsilon_i/\gamma}}{\sum_i \mathrm{e}^{-\epsilon_i/\gamma}}. \tag{5}$$

To evaluate γ, Eyring would turn to the Law of Dulong ad Petit that the heat capacity of a mole of metal was 6.2 cal/degree, noting that this was the case for all metals in the classical range where $\gamma \gg h\nu$. For a metal atom oscillating with three degrees of freedom, the temperature coefficient would be

$$k = \frac{(6.2 \text{ cal/mole degree})\,(4.184 \times 10^7 \text{ erg/cal})}{(3 \text{ degrees of freedom/atom})(6.023 \times 10^{23} \text{ atoms/mole})}$$

$$\simeq 1.4 \times 10^{-16} \text{ erg/deg} \tag{6}$$

for each degree of freedom. This is, of course, an estimate of the Boltzmann's constant, 1.38×10^{-16} erg/deg, and therefore the average energy for each degree of freedom is simply kT. This then gives the Boltzmann's equation,

$$P_i = \frac{N_i}{N_0} = \frac{e^{\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}, \tag{7}$$

where N_i is now the number of atoms or molecules with energy ϵ_i and

$$N_0 \left(= \sum_i N_i \right)$$

is the total number of such species. The average energy, E, for the system becomes

$$E = \sum_i \epsilon_i P_i = \frac{\sum_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}} \equiv kT^2 \left(\frac{\partial \ln \sum_i e^{-\epsilon_i/kT}}{\partial T} \right)_V, \tag{8}$$

where the identity can be verified by carrying out the partial differentiation with respect to temperature with all other variables constant. The summation over energy states

$$\sum_i e^{-\epsilon_i/kT}$$

is called the partition function, f, and just as the energy itself can be separated into translational, rotational and vibrational degrees of freedom, i.e.,

$$\epsilon_i = \epsilon_t + \epsilon_r + \epsilon_v, \tag{9}$$

so to can be the partition function, i.e.,

$$f = \sum_{t,r,v} e^{-\epsilon_t/kT} e^{-\epsilon_r/kT} e^{-\epsilon_v/kT} = f_t f_r f_v. \tag{10}$$

Now in order to discuss Eyring's models in research it is necessary to have explicit expressions for the partition functions particularly the translational and vibrational. For example, in the development of Eyring's activated complex theory of chemical reactions, it is a vibrational degree of freedom that converts to translational degrees of freedom as the activated complex separates into either products or reactants and in the

development of Eyring's significant structure theory of liquids it is the proper combination of solid and gaslike degrees of freedom that is required. Additionally, we require bridging between statistical mechanics and thermodynamics in order to express his molecular theory of the liquid state in terms of observable thermodynamic quantities. This was the Eyring approach to developing and testing a physical–chemical theory.

The translational partition function: The translational energy may be obtained using the Wilson–Sommerfeld quantization rule from old quantum theory in which

$$\oint m\dot{x}\,\mathrm{d}x = nh, \tag{11}$$

where the translation is in the x direction, the integral is over the complete cycle, and m, $\dot{x}$, n, and h are the mass, the velocity in the x direction, an integer for the translational energy states and Planck's constant, respectively. For a complete cycle over the dimension a,

$$nh = m\dot{x}a - m(-\dot{x})a = 2m\dot{x}a, \tag{12}$$

but the kinetic energy is

$$\epsilon_x = \frac{1}{2}m\dot{x}^2 = \frac{1}{2}m\,\frac{n^2h^2}{4m^2a^2} = \frac{n^2h^2}{8ma^2} \tag{13}$$

and

$$f_{t(x)} = \sum_{n=1}^{\infty} \mathrm{e}^{-n^2h^2/8ma^2kT}, \tag{14}$$

which on integration gives

$$f_{t(x)} = \int_0^{\infty} \mathrm{e}^{-n^2h^2/8ma^2kT}\,\mathrm{d}n = \frac{(2\pi mkT)^{1/2}a}{h}. \tag{15}$$

Equation 15 is the one-dimensional translational partition function through the distance a. For the three translational degrees of freedom,

$$f_t = f_{t(x)}f_{t(y)}f_{t(z)} = \sum_n \mathrm{e}^{-(\epsilon_x+\epsilon_y+\epsilon_z)/kT} = \frac{(2\pi mkT)^{3/2}V}{h^3} \tag{16}$$

giving an expression that can be evaluated for a given mass, temperature, and volume. The sum overstates for N indistinguishable gas molecules must be divided by $N!$ so that the translational partition function for N gas molecules, f_g^N, is $(f_t e/N)^N$.

The rotational partition function: The rotational energy is

$$\epsilon_r = \frac{J(J+1)h^2}{8\pi^2 I}, \tag{17}$$

where J is the quantum number and

$$I = \sum_i m_i x_i^2$$

is the moment of inertia. Appropriately considering degeneracy and symmetry factors, σ,

$$f_{2r} = \frac{8\pi^2 IkT}{\sigma h^2} \tag{18}$$

for a two-dimensional rotator and for a three-dimensional rotator is the following:

$$f_{3r} = \frac{8\pi^2(8\pi^3 \boldsymbol{ABC})^{1/2}(kT)^{3/2}}{\sigma h^3} \tag{19}$$

where $\boldsymbol{A}$, $\boldsymbol{B}$, and $\boldsymbol{C}$ are the moments of inertia along the three principal axes of the rotator.

The vibrational partition function: A harmonic oscillator absorbs energy in units of $h\nu$ such that the partition function for one degree of vibrational freedom is written

$$f_{1\nu} = \sum_{n=0}^{\infty} e^{-nh\nu/kT} = e^{-0/kT} + e^{-h\nu/kT} + e^{-2h\nu/kT} + \cdots \tag{20}$$

Substituting x for $e^{-h\nu/kT}$ gives

$$f_{1v} = 1 + x + x^2 + \cdots = \frac{1}{1-x} = (1 - e^{-h\nu/kT})^{-1} \tag{21}$$

For many vibrational degrees of freedom,

$$f_v = \prod_i (1 - e^{-h\nu_i/kT})^{-1}. \tag{22}$$

Bridging statistical mechanics and thermodynamics: The experimental variables in the above partition functions for a closed system are T and V and the thermodynamic quantity that is a function of these variables is the Helmholtz free energy or work function, A,

$$A = E - TS \tag{23}$$

and

$$dA = -S\,dT - P\,dV, \tag{24}$$

where S is entropy and P is pressure. It can be shown that

$$E = -T^2\left(\frac{\partial(A/T)}{\partial T}\right)_V \tag{25}$$

such that by Eq. 8,

$$\left(\frac{\partial(A/T)}{\partial T}\right)_V = -k\left(\frac{\partial \ln \sum_i e^{-\epsilon_i/kT}}{\partial T}\right)_V. \tag{26}$$

On integration and proper evaluation of the integration constant, A becomes a simple

function of the partition function,

$$A = -kT \ln \sum e^{-\epsilon_i/kT} = -kT \ln(f). \tag{27}$$

The other eight thermodynamic functions, in addition to E and A, can now be written in terms of f. By Eqs. 24 and 27,

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln(f)}{\partial V}\right)_T \tag{28}$$

and

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = k\left(\frac{\partial [T \ln(f)]}{\partial T}\right)_V. \tag{29}$$

The Gibbs free energy, G, is

$$G = A + PV = -kT \ln(f) + VkT\left(\frac{\partial \ln(f)}{\partial V}\right)_T \tag{30}$$

and the enthalpy is

$$H = E + PV = kT^2\left(\frac{\partial \ln(f)}{\partial T}\right)_V + VkT\left(\frac{\partial \ln(f)}{\partial V}\right)_T. \tag{31}$$

The heat capacity at constant volume, C_v, is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = k\left(\frac{\partial}{\partial T}\frac{T^2 \partial \ln(f)}{\partial T}\right)_V. \tag{32}$$

The coefficient of thermal expansion, α, becomes

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\frac{\left[\frac{\partial (kT)}{\partial T}\left(\frac{\partial \ln(f)}{\partial V}\right)_T\right]_V}{kT\left(\frac{\partial^2 \ln(f)}{\delta V^2}\right)_T}. \tag{33}$$

The coefficient of volume expansion, β, is written

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left[kT\left(\frac{\partial^2 \ln(f)}{\partial V^2}\right)_T\right]^{-1} \tag{34}$$

and finally the heat capacity at constant pressure, C_p,

$$C_p = C_v + \frac{\alpha^2 VT}{\beta}, \tag{35}$$

which by making the substitutions of Eqs. 32, 33, and 34 is also obtained in terms of $\ln(f)$. It was in using this set of equations, 8 and 27 through 35, that Eyring tested and developed his significant structure theory of liquids.

Look at what has been achieved in the short Eyring formulation. One gains a sense of the probability of occurrence of a state as being expressible in terms of its energy in relation to the sum of the energies of all other possible states. It does not matter what the states are. It could be the relative probabilities of reactants and products or reactants and any rare state, e.g., the activated complex that occurs on going from reactants to products. It is seen that descriptions on the atomic and molecular level can be translated into observable thermodynamic properties. Even the fundamental constant, the Boltzmann's constant, has been evaluated from a simple experimental result. The foregoing, as well as what follows, is, of course, only a sketch. The original writings of Eyring and his colleagues should be consulted for a more complete perspective and to see more accurately how each basic element is covered in his unique fashion. Even his writings, however, could not match in effectiveness an Eyring lecture for conveying a sense of the power of this discipline that he understood in such depth.

3. EYRING'S CONTRIBUTION TO POLYMER CHEMISTRY AND THE PROBLEM OF THE ACCESSIBILITY OF REGIONS OF PHASE SPACE HAVING THE SAME ENERGY

In the 1969 review of his models of research [4], Eyring began with a section entitled "The Not So Random Walk Problem." This drew on his 1932 paper [5], which demonstrated the means of calculating the mean square electric moment for large flexible molecules having numerous electric dipole moments and which also provided a means of calculating the mean square length between the ends of a flexible chain. The expression for a given chain configuration for the square of the length of a resultant vector, C, was given as

$$C^2 = \sum_{j=1}^{n} C_{xj}^2 + 2 \sum_{j=1}^{n} \sum_{s<j} [(C_{xj} e_{xj}) \cdot (A_j' \ldots A_s' C_{xs} e_{xs})], \tag{36}$$

where C_{xj} are the magnitude and sign of the component vectors in the x_j direction; A_j' is the reverse of the transformation of the j to $j-1$ coordinate system. The average property, C_a^2, for a collection configurations was then to be obtained as

$$C_a^2 = \frac{\int C^2 \, e^{-E/kT} \sin(\theta_2) \, d\theta_2 \ldots \sin(\theta_m) \, d\theta_m \, d\phi_2 \ldots d\theta_m}{\int e^{-E/kT} \sin(\theta_2) \, d\theta_2 \ldots \sin(\theta_m) \, d\theta_m \, d\phi_2 \ldots d\phi_m}, \tag{37}$$

where θ_j is the angle between two consecutive vectors and ranges from 0 to π, the ϕ_j range from 0 to 2π (see Fig. 1A), and E is a function of the θ_j and ϕ_j. When the vectors are the distances between atoms instead of the electric moments, the root mean square distance, C_a, between the ends of the chain molecule is obtained. This is fundamental to the theory of high polymers. When applied to polypeptides and proteins the vector has been taken as the distance between successive α-carbons in the chain [6].

The primary Eyring message with respect to these considerations [4], however, derives from its limitations, i.e., the analysis is complicated by the occurrence of excluded configurations as when a chain would cross its own path (see Fig. 1B). Because of this, the generation of configurations for a flexible chain can not be a truly random walk process. A subsequent segment of a chain cannot occupy the same space as a former segment. There is also the problem of accessibility of configurations of equal energy. For example, if the nonallowed configuration of two chain segments occupying the same space in Fig. 1B were removed such that the $j-1$ segment is above the $j+4$ segment then there becomes the problem of the accessibility of an equivalent energy

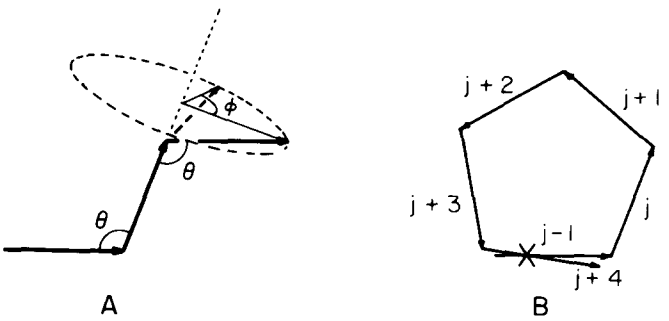

Fig. 1. (A) Definitions of the angles θ and ϕ used in generating the configurations of a flexible chain. The vectors can be the dipole moments within segments of the chain or the lengths representing segments. (B) A disallowed configuration in which chain segments $j-1$ and $j+4$ would occupy the same space.

state with the $j+4$ segment above the $j-1$ segment. In a fiber of concentrated chains the problem becomes particularly severe. Now going from $3N$-dimensional configuration space to $6N$-dimensional phase space where conjugate momenta are also specified for each atom, there is the analogous concern of the validity of the ergodic hypothesis which requires "that an isolated mechanical system will visit, with equal frequency, all parts of phase space have the same energy" [4]. In view of this early (1932) concern of generating polymer chain configurations (Eq. 36) and calculating average properties (Eq. 37) coupled with the problem of the frequency of visiting equal regions of phase space, perhaps it is not surprising that Eyring would direct his major efforts toward better understanding rate processes, which in this context could be concern for the rate or frequency at which equal volumes of phase space may be accessed.

4. EYRING'S ABSOLUTE REACTION RATE THEORY

The model in absolute reaction rate theory is one of interacting or reacting species colliding with their kinetic energies being converted into potential energy. When the relative orientation of colliding species is correct and when their kinetic energies along

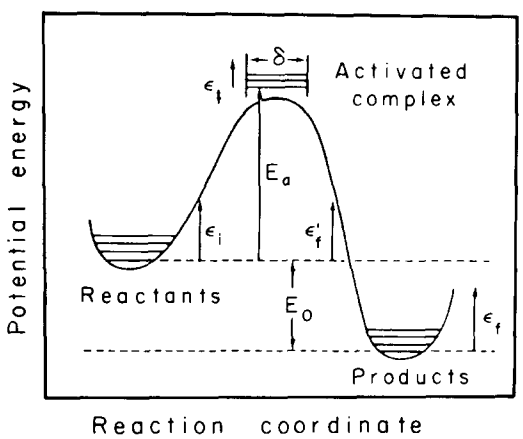

Fig. 2. Schematic potential energy profile for the interconversion of reactants and products plotted along the reaction coordinate. The difference in potential energy between reactants and activated complex is E_a and between reactants and products is E_0. ϵ_i, $\epsilon_\ddagger$, and ϵ_f are the energy states of the reactants, the activated complex, and the products, respectively. δ is the length along the reaction coordinate through which the activated complex exists.

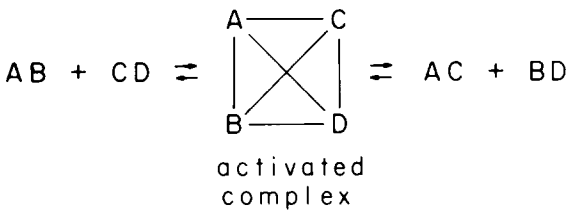

Fig. 3. Reaction of two diatomic molecules, *AB* and *CD* combining to form an activated complex and dissociating to products *AC* and *BD*.

the line of reaction is great enough then there is sufficient potential energy to achieve the activated complex. The potential energy along the reaction coordinate is shown in Fig. 2, where the several energies of interest are defined. These energies are used in writing the several partition functions required in formulating Eyring's absolute reaction rate theory. It was at this stage in Eyring's development of his rate theory where his descriptions of the reaction coordinate in terms of the mountain passes and valleys of Utah provided one of the most memorable of picturesque visualizations. He would often draw on the barometric formula and picture molecules drifting over a mountain pass.

Eyring's rate theory has been applied to processes ranging from diverse chemical reactions to a complete range of transport and deformation processes [2, 6–11]. It is most commonly derived, however, using the example of bimolecular reactions of diatomic molecules as shown in Fig. 3. This will follow, along with an application to the process of transmembrane ion transport by means of the channel mechanism.

Derivation of the rate equation

The phenomenological statement of the forward velocity of a rate process, ν_f, is written

$$\nu_f = \kappa \frac{1}{2} \frac{N^\ddagger}{V} \frac{\bar{u}}{\delta}, \tag{38}$$

where $N^\ddagger$ is the number of activated complexes in the volume, V, and $\bar{u}$ is the mean velocity with which the activated complex moves through the distance δ at the top of the potential barrier. The factor 1/2 is because at equilibrium exactly one half of the complexes are moving in the forward direction and κ is the transmission coefficient which is to introduce special cases such as tunneling which occurs when the barrier is steep and narrow. The average velocity, following Eq. 8, is written

$$\bar{u} = \sum_i u_i P_i = \frac{\sum_i u_i \, e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}. \tag{39}$$

Rewriting Eq. 11 with $u = \dot{x}$, then Eq. 13 for the length $a = \delta$ becomes

$$\epsilon_i = \frac{1}{2} m^\ddagger u^2 = \frac{n^2 h^2}{8 m^\ddagger \delta^2}. \tag{40}$$

Substituting Eq. 40 into Eq. 39 and integrating gives the simple result

$$\bar{u} = \left(\frac{2kT}{\pi m^\ddagger}\right)^{1/2}. \tag{41}$$

Following Eq. 7, the ratio of the probability of the activated complex, $P^{\ddagger}$, to the initial state, P_i, is

$$\frac{P^{\ddagger}}{P_i} = \frac{N^{\ddagger}}{N_1 N_2} = \frac{\sum_{\ddagger} e^{-\epsilon^{\ddagger}/kT} e^{-Ea/kT}}{\sum_{i} e^{-\epsilon_i/kT}}, \tag{42}$$

where N_1 and N_2 are the numbers of molecules of AB and CD, respectively, and the energies $\epsilon^{\ddagger}$, ϵ_i, and E_a are defined in Fig. 2. Writing the translational, rotational, and vibrational partition functions (using Eqs. 16, 19, and 22) for the activated complex and dividing out the volume, V, from the translational partition functions yields

$$\frac{N^{\ddagger}/V}{(N_1/V)(N_2/V)} = \frac{\left[(f_t/V) f_{3r} \dfrac{(2\pi m^{\ddagger} kT)^{1/2}\delta}{h} \prod_{i=1}^{5} (1 - e^{-h\nu_i/kT})^{-1}\right] e^{-E_a/kT}}{(f_1/V)(f_2/V)}, \tag{43}$$

where f_1 and f_2 are the complete partition functions for the diatomic molecules and f_t and f_{3r} are defined in Eqs. 16 and 19, respectively.

With four atoms in the activated complex, there are twelve degrees of freedom: three translational, three rotational, one special vibration which becomes the translational degree of freedom through the distance δ, and five vibrational degrees of freedom. Factoring out the special translational degree of freedom which is unique to an activated complex about to separate by a translation into two parts; rewriting (N_1/V) and (N_2/V) as simply $[AB]$ and $[CD]$, i.e., the concentrations of the reactants, and defining the remainder of the partition functions and $e^{-E_a/kT}$ as $K^{\ddagger}$ gives

$$\frac{N^{\ddagger}}{V} = [AB][CD] \frac{(2\pi m^{\ddagger} kT)^{1/2}\delta}{h} K^{\ddagger}. \tag{44}$$

Substituting Eqs. 44 and 41 into Eqs. 38, the statement of the forward reaction rate becomes

$$\nu_f = \kappa \frac{1}{2} [AB][CD] \frac{(2\pi m^{\ddagger} kT)^{1/2}\delta K^{\ddagger}}{h} \left(\frac{2kT}{\pi m^{\ddagger}}\right)^{1/2} \frac{1}{\delta} \tag{45}$$

or

$$\nu_f = [AB][CD]\kappa \frac{kT}{h} K^{\ddagger}. \tag{46}$$

The specific rate constant k', therefore, is

$$k' = \kappa \frac{kT}{h} K^{\ddagger}. \tag{47}$$

Thermodynamic Form of the Absolute Reaction Rate Equation: The thermodynamic form of the absolute reaction rate equation derives from a typical Eyring insight. $K^{\ddagger}$ is what would be written as the equilibrium constant for the combination of reactants to form any complex, whether long lived or fleeting and whether at high or extremely low concentrations, with the exception that the unique translational degree of freedom has

been factored out. But since δ cancels out in Eq. 45, this length is defined as is most convenient. Eyring made the definition

$$\delta = \frac{h}{(2\pi m^{\ddagger} kT)^{1/2}} \tag{48}$$

such that the quantity factored out of the product of partition fractions becomes unity and direct analogy is drawn to the thermodynamic properties of equilibrium processes with the parallel set of relationships that since

$$\Delta G = -RT \ln(K)$$

then

$$\Delta G^{\ddagger} = -RT \ln (K^{\ddagger}). \tag{49}$$

Also since

$$\Delta G = \Delta H - T\,\Delta S$$

then

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\,\Delta S^{\ddagger}. \tag{50}$$

Accordingly, the specific rate constant becomes

$$k' = \kappa \frac{kT}{h} e^{-\Delta G^{\ddagger}/RT} \tag{51}$$

and

$$k' = \kappa \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}. \tag{52}$$

With the thermodynamic form of the rate equation it becomes possible to consider directly the Gibbs free energy of activation, $\Delta G^{\ddagger}$, the enthalpy of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$. In addition to the considerable interest in these thermodynamic quantities themselves, they make it possible to introduce other effects correctly such as the effects of pressure on a process and of an applied potential on the transport process of a charged species. For example, the effects of pressure can be treated since

$$\left(\frac{\delta \Delta G^{\ddagger}}{\delta P}\right)_T = \Delta V^{\ddagger} \tag{53}$$

and the total free energy change, $\Delta G_t^{\ddagger}$, with respect to a reference pressure, P_1, becomes

$$\Delta G_t^{\ddagger} = \Delta G^{\ddagger} + \overline{\Delta V}^{\ddagger}(P_2 - P_1), \tag{54}$$

where $\overline{\Delta V}^{\ddagger}$ is the mean volume change on forming the activated state. Also the total free energy change of a transport process due to an applied potential, E, is written

$$\Delta G_t^{\ddagger} = \Delta G^{\ddagger} + zFE, \tag{55}$$

where z is the charge on the transported species and F is the Faraday constant. Significantly with the Eyring formalism the plot of the free energy profile becomes a complete description of the rate process. This will be demonstrated below with a now-described channel mechanism of monovalent cation transport across lipid membranes.

Steady State Reaction Networks: Ion Transport Across Lipid Membranes by Means of a Channel Mechanism: In 1949 [12, 13], and subsequently with a number of publications [7, 14], Eyring applied rate theory to the important biological problem of ion transport across cell membranes. As the discrete molecular structures and their contributions to the macroscopic current were not known until the last few years, the formalism was given in general terms. With the Eyring formalism, it is now possible to describe the mechanism in detail of the first channel of known molecular structure. The Eyring formalism is required to plot the free energy profile and to introduce the voltage dependence and it will be seen that the free energy profile along the permeation coordinate allows calculation of the ion currents passing through a single channel over wide ranges of ion concentrations and transmembrane potentials.

The Gramicidin A transmembrane channel is shown in Fig. 4 in terms of a space filling model [15]. It is a dimer with two identical polypeptide molecules joining together midway through the lipid membrane by means of six hydrogen bonds. The association of the two polypeptide chains is amino end to amino end and the two molecules can be covalently joined in the channel structure by means of a malonyl bridge, $-CO-CH_2-CO-$,

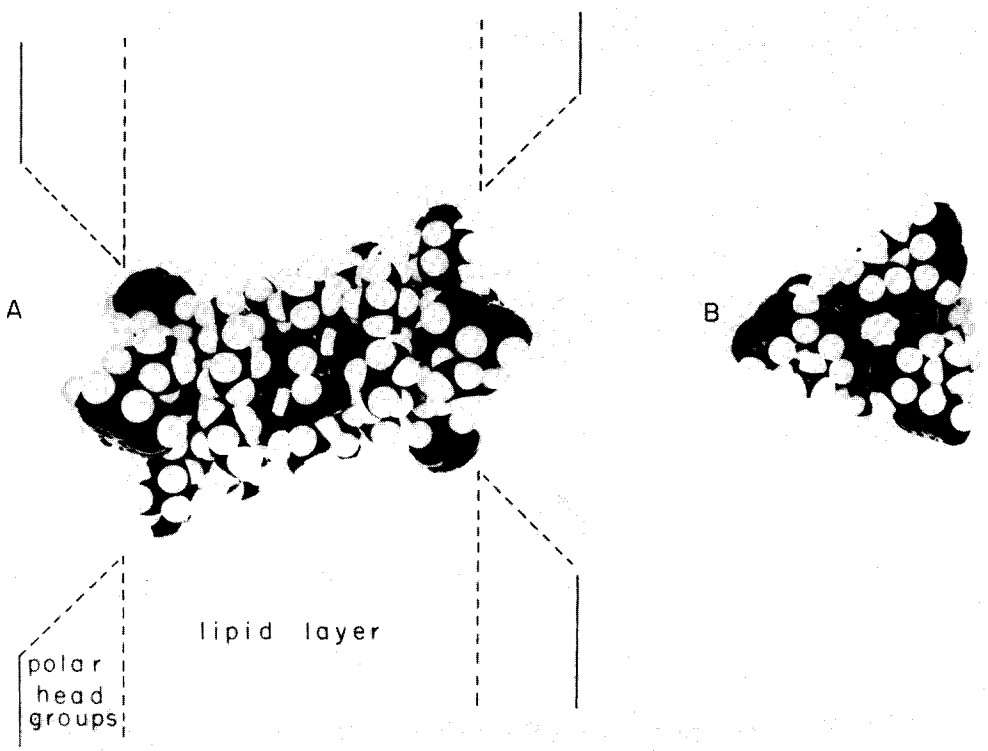

Fig. 4. Gramicidin A transmembrane channel. (A) Side view showing the structure spanning the lipid layer of a membrane. (B) Channel view showing the 4 Å diameter channel.

between the amino ends. The structure is a left-handed β-helix with 6.3 residues per turn resulting in a water-filled 4 Å diameter channel through which only monovalent cations can pass. The 26 Å long channel spans from one side to the other of a lipid membrane whether it be an artificial bilayer or part of a cell membrane. It has been shown that there are two ion binding sites in the channel separated by just over 20 Å and related by a twofold symmetry axis [16, 17]. The steady-state scheme for a two site model is given in Fig. 5A which defines the rate constants and in Fig. 5B are the appropriate steady-state equations, where $\dot{\chi}_i$ is the rate of change for each occupancy state, i.e., *oo*, *ox*, *xo*, *xx*.

In the absence of an applied potential, sodium-23 nuclear magnetic resonance has been used to determine the two binding constants, one for the tight site for forming the two equivalent states *xo* and *ox* and one for the weak binding site for the second ion binding, i.e., $ox \rightarrow xx$, and the off rate constants, k^t_{off} and k^w_{off}, were determined for single and double occupancy [18, 19]. In addition, dielectric relaxation studies have been used to estimate the rate constant for jumping over the central barrier, k_{cb} [20]. Thus in the absence of an applied potential all the relevant rate constants have been determined. Using the thermodynamic form of the Eyring rate equation (Eq. 51) with the transmission coefficient taken as unity, the free energy can be plotted as a function of the distance along the channel. This is shown as the solid line in Fig. 5C for a single ion passing through the channel. The dashed line is for double occupancy. Actually in drawing the curves only the maxima are defined. This issue has already been dealt with by Eyring in the statement, "In describing multi-barrier kinetics, one should note that the free energy potential profiles have significance only at the minima and at the activated states. The shapes of the curves relating these maxima and minima do not play an important part in the cases considered here, since the entropy in the region connecting a minimum and an activated state is of no interest and is undefined" [21].

On addition of the transmembrane potential, Eq. 55 is rewritten

$$\Delta G_t^{\ddagger} = \Delta G^{\ddagger} + \frac{lzFE}{2dRT} \tag{56}$$

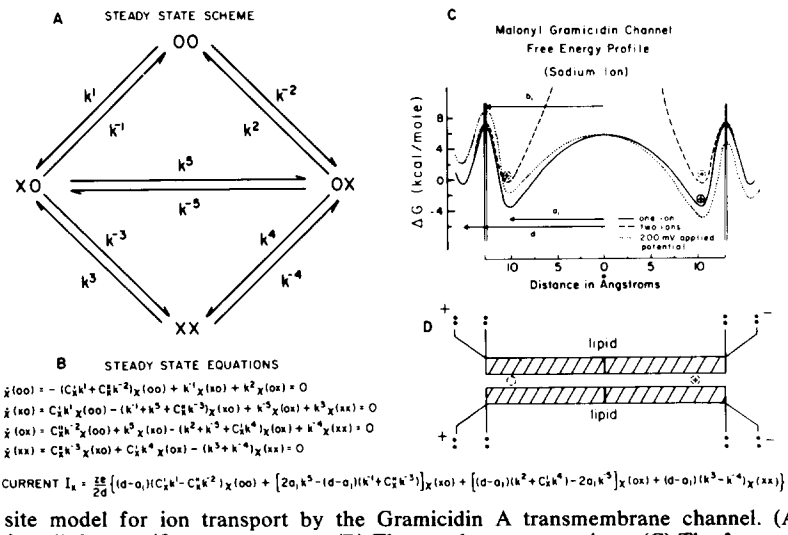

Fig. 5. Two site model for ion transport by the Gramicidin A transmembrane channel. (A) Steady-state schemes defining all the specific rate constants. (B) The steady-state equations. (C) The free energy profile for sodium ion movement through the channel. The barrier heights are defined by the thermodynamic form of Eyring's absolute reaction rate theory. (D) Schematic view of the channel to be compared with part C. (E) Complete expression for the single channel current. See text for discussion. Adapted from Refs. 18 and 19.

where $2d$ is the total distance across which the potential, E, is applied and l is the distance along the channel from a minimum to the next barrier. This assumes that the potential gradient across the membrane is linear which is reasonable due to the uniformity of the structure (see Fig. 4A). Defining $X \equiv \exp(zFE/2dRT)$, the power to which X is raised is the relevant length as defined in Fig. 5C. The resulting voltage dependent rate constants are given in Fig. 6 (recognizing that the on-rate constants are obtained from the product of the relevant binding and off-rate constants). With the rate constants as defined in Fig. 6 and the experimental values for k^l_{off}, etc. [18, 19], the free energy profile for a given transmembrane potential can be plotted, as is done in the dotted curve of Fig. 5C for a 200 mV transmembrane potential.

It is possible to observe experimentally the current due to the formation of a single channel as first demonstrated by Hladky and Haydon [22] and this value can be plotted as a function of ion concentration and for different transmembrane potentials as is done in Fig. 7 for the malonyl Gramicidin channel. Recognizing that the experimental values of the rate constants have an expected error of a factor of 2 or 3, a calculation, of the single channel currents with the experimental values optimized by a least squares best fit to all potentials simultaneously, was carried out. The result is given as the solid lines in Fig. 7. It is important to know that, in achieving the best fit to the experimental points, the equilibrium derived rate constants varied only within the expected experimental error and that a single set fit the curves for all of the applied potentials [19]. Thus, using Eyring's rate theory to introduce voltage dependence, the experimental single channel currents have been calculated with rate constants derived in absence of the applied field. Most significantly, the simple free energy profile calculated using the thermodynamic form of Eyring's rate equation is all that is required to calculate single channel currents over wide ranges of ion concentrations and of transmembrane potentials. This is just a recent of many possible demonstrations of the power and usefulness of Eyring rate theory.

Irreversible Thermodynamics. The Coupling of Chemical Reactions and Onsager's Reciprocal Relations: Another Eyring insight comes with the application of absolute reaction rate theory to irreversible thermodynamics. He has stated the following postulates [4]:

"Because activated complexes are isolated from each other, stopping the backward elementary reaction, by removing products, leaves the forward rate unchanged to a useful approximation."
"It follows that the specific rate of a forward elementary reaction, at equilibrium may be used as the specific rate for a non-equilibrium situation."

$$k^1 = k^t_{on}\, X^{(d-b_1)}, \quad k^{-1} = k^t_{off}\, X^{-(b_1-a_1)}, \quad k^2 = k^t_{off}\, X^{(b_1-a_1)},$$

$$k^{-2} = k^t_{on}\, X^{-(d-b_1)}, \quad k^3 = k^w_{off}\, X^{(b_1-a_1)}, \quad k^{-3} = k^w_{on}\, X^{-(d-b_1)},$$

$$k^4 = k^w_{on}\, X^{(d-b_1)}, \quad k^{-4} = k^w_{off}\, X^{-(b_1-a_1)}, \quad k^5 = k_{cb}\, X^{a_1} \text{ and}$$

$$k^{-5} = k_{cb}\, X^{-a_1}$$

$$X \equiv \exp(zFE/2dRT)$$

Fig. 6. Introduction of voltage dependence to the equilibrium derived rate constants. The lengths a_1, b_1, and d are defined in Fig. 5C.

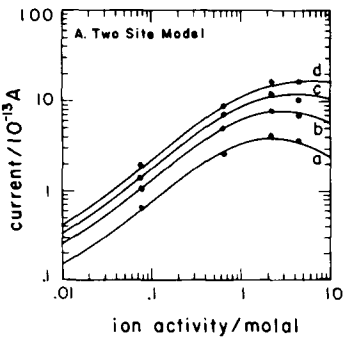

Fig. 7. Plots of single channel currents as a function of molal activity of sodium ion. Curves *a*, *b*, *c*, and *d* are 50, 100, 150 and 200 mV transmembrane potentials, respectively. The dots are the experimental values and the solid lines are the calculated curves (from Ref. 19).

Starting with the Eyring general flux statement for a series of $n-1$ barriers

$$J = k_0 \frac{C_0\lambda_0 - C_n\lambda_n\, e^{-\Delta G_n/RT}}{1 + \sum_{i=1}^{n-1} e^{\delta G_i^{\ddagger}/RT}}, \tag{57}$$

where the quantities are defined in Fig. 8. Now an applied potential is introduced and a Maclaurin expansion is carried out on the exponentials for the case where zFE is smaller than RT to give

$$J = \frac{\lambda_0 k_0}{n}\left(C_0\, e^{zFE/2RT} - C_n\, e^{-zFE/2RT}\right), \tag{58}$$

where n is the number of barriers. Again expanding the exponentials, keeping only the first two terms and defining $P^0 = \lambda_0 k_0/n$ gives

$$J = P^0\left[(C_0 - C_n) - \frac{1}{2}(C_0 + C_n)\frac{zFE}{RT}\right]. \tag{59}$$

Replacing concentrations by activities, a_0 and a_n, defining a mean activity, $\bar{a} = 0.5(a_0 + a_n)$ and including the activity coefficient γ_0 with the definition that $P^0 = P/\gamma_0$

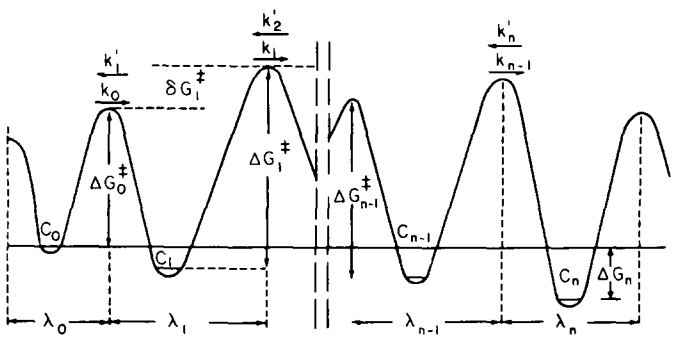

Fig. 8. Schematic of a free energy profile for the series of barriers encountered as an ion passes through a membrane. The λ_i are lengths between barriers. The $\Delta G_i^{\ddagger}$ are the Gibbs free energies of activation. $\delta G_i^{\ddagger}$ are the differences between maxima referred back to the first barrier. Adapted with permission from Ref. 3.

yields

$$J = -P^0\bar{a}\left(\frac{\delta\bar{a}}{\bar{a}} + \frac{zFE}{RT}\right).$$

The desired expression is obtained on demonstrating that the change in chemical potential $\delta\mu$ divided by RT is equal to $\delta\bar{a}/\bar{a}$ such that

$$J = \frac{-P^0\bar{a}}{RT}(\delta\mu + zFE). \tag{61}$$

For the process of transport across a membrane $\delta\mu$ and E, each divided by the membrane thickness, are the forces driving the flux. Using this expression, Eyring was able to derive Onsager's reciprocal relations for irreversible processes. The example employed was carrier facilitated transport of an ion across a membrane. The three fluxes were the ion, J_1, the carrier, J_2, and the charge, J_3, and the three forces were due to the chemical potential of the ion, X_1, of the carrier, X_2, and the electrical potential, X_3. Thus, absolute reaction rate theory, when the exponentials are expressed as an infinite series and only the first linear term is kept, gives rise to familiar relations of irreversible thermodynamics.

It is common that a superficial look can give the appearance of paradox or contradiction. So too can the casual observation of Eyring rate theory and its applications give that appearance. To the casual viewer, equilibrium theory is used in the derivation of the thermodynamic form of the rate equation, yet rate theory is applied to nonequilibrium thermodynamics. While in the preceding sketch the statistical mechanical formulation of equilibrium constants was not given, Eyring would routinely do this prior to the derivation of the rate equation. In doing so, he would make clear the fundamental formalism. Both formulations start with the ratios of the probabilities of the states of interest and the ratios of probabilities of states are given in terms of the ratios of the products of the partition functions describing the states. With the appropriate definition of the length for the unique translational degree of freedom of the activated complex such that its being factored out leaves the remaining product unchanged, what remains is that which would be written for the equilibrium constant between reactants and any achievable state with the exception that there is one less vibrational degree of freedom. Since it would be a high energy vibrational state, it would contribute least to the magnitude of the vibrational partition function. Obviously the thermodynamic form of the rate equation provides a sound statement. It is equally clear that one activated complex does not communicate through space to another activated complex, such that activated complexes derived from reactants are unaware of the absence or presence of activated complexes derived from products. Accordingly, instantaneous removal of activated complexes derived from products would not affect the rate of activated complexes formed from reactants. All other things being constant, the concentration of activated complexes formed from reactants is determined only by the concentration of reactants and the specific rate constant. It would seem apparent that absolute reaction rate theory can be applied to irreversible processes.

5. EYRING'S SIGNIFICANT STRUCTURE THEORY OF LIQUIDS [23]

The significant structure theory of liquids is classic Eyring. It draws on the law of rectilinear diameters which states that the mean density of a liquid and its equilibrium vapor is one-half the density of the solid at its melting point and is a linear function of

temperature, decreasing to one-third the melting point density of the solid at the critical temperature. To Eyring, this law meant that the liquid could be represented as having as many holes of approximately molecular size as there are molecules in the gas phase and that these holes or fluidized vacancies conferred gaslike degrees of freedom on molecules surrounding each hole. By means of a neighboring molecule jumping into a hole, the hole moves around in the liquid just about as freely as molecules move through the gas phase. "The vapor is thus mirrored in the liquid as fluidized vacancies" [4]. The energy to form a vacancy is the energy of vaporization. The volume of expansion on melting is a measure of the number of fluidized vacancies. Thus the liquid partition function is represented as the products of properly weighted translational and vibrational partition functions. The ratio of the volume of the solid, V_s, over the volume of the liquid, V, gives the mole fraction of solidlike degrees of freedom and $(V - V_s)/V$ the mole fraction of gaslike degrees of freedom. Thus,

$$f = (f_s')^{NV_s/V}(f_g)^{N(V-V_s)/V} \tag{62}$$

with

$$f_g = \frac{(2\pi mkT)^{3/2}eV}{h^3N} \tag{63}$$

and

$$f_s' = \left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3}\right]\left(1 + n\,\frac{V - V_s}{V_s}\,e^{-aE_sV_s/(V-V_s)RT}\right), \tag{64}$$

where E_s is the molal energy of sublimation and θ is the Einstein characteristic temperature. The second term in Eq. 64 arises due to a positional degeneracy conferred on molecules by the presence of fluidized vacancies, but the additional positions are only available to molecules with sufficient energy which is proportional to the energy of sublimation divided by the mole fraction of fluidized vacancies. The quantities n and a are proportionality factors to be calculated. And indeed Eyring could calculate the magnitude of these quantities for the liquid of interest. With V_m as the volume of the liquid at the melting point, the relationship for n was

$$n\,\frac{V_m - V_s}{V_s} = z\,\frac{V_m - V_s}{V_m}, \tag{65}$$

where z is the number of neighboring positions. For argon with $z = 12$ and $V_m/V_s = 1.12$, $n = 10.7$ and the best fit value was 10.8. A slightly more complex relation would give an a of 0.0052 for argon whereas the best fit value was 0.00534. Thus, Eyring developed a liquid theory which he demonstrated could calculate the many thermodynamic quantities derived in Sec. II, e.g., see Eqs. 27 through 35.

It was in developing the significant structure theory of liquids that two aspects of the practical side of this theoretical chemist were so apparent. As the calculations proceeded he would, of course, regularly compare calculated results with experimental results and would often say that "A theoretical chemist who doesn't keep an eye on the experimental results is like a pilot who doesn't know where the ground is." The second aspect was the satisfaction that Eyring would gain from the ability of his liquid theory to calculate the thermodynamic quantities of liquids and the comfort which he would take in noting that no other theory of the liquid state, however esoteric, could do so well. His goal was

to develop a useful liquid theory and this, of course, he accomplished with the application to many liquids [23].

6. EYRING'S ONE ELECTRON THEORY OF OPTICAL ROTATION

Historically the theory of optical rotation has had two schools of thought: the Kirkwood polarizability or coupled oscillator theory and the Eyring one electron theory both of which appeared in 1937 [24, 25]. The one electron theory, as we have come to appreciate with the Eyring approaches, begins with an elegantly simple model: a single chromophoric electron represented as a three-dimensional harmonic oscillator in the presence of a perturbing potential. The potential for the chromophoric electron is then written

$$V = \tfrac{1}{2}(k_1x^2 + k_2y^2 + k_3z^2) + Axyz. \tag{66}$$

The chromophoric ellipsoid is anisotropic with $k_1 > k_2 > k_3$ and the perturbing potential, $Axyz$, provides the dissymmetry. This provided for the first octant rule in optical rotation because the direction of rotation of plane polarized light followed the sign of A times the sign of the octant in which the perturbing potential occurred. If an uncharged vicinal group with incompletely screened nuclei or a positively charged group were in a positive octant then the rotation of plane polarized light would be positive. The application of this theory to 3(+) methyl cyclopentanone is shown in Fig. 9 for the $n - \pi^*$ transition of the carbonyl chromophore. With the coordinate system properly set up according to the relative magnitude of the k_i, the methyl group is in a positive octant and the sign of the rotation for this structure is positive [26]. Indeed using this theory Eyring and his colleagues were able to predict absolute configuration [27].

While for many years there was an active controversy as to which theory (the polarizability or one electron) was correct, it turned out, as effectively demonstrated by

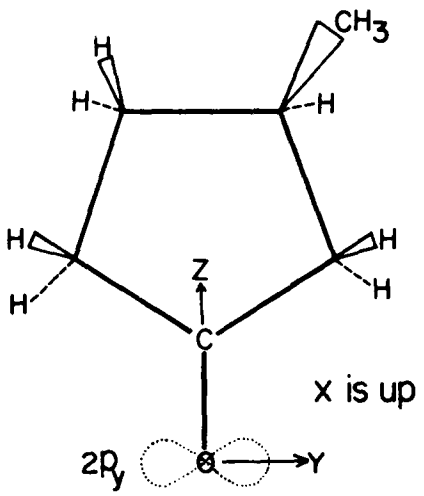

Fig. 9. Structure of 3(+) methyl cyclopentanone. The coordinate system has its origin at the oxygen atom where the nonbonding orbitals for an $n - \pi^*$ transition are located. The right-handed coordinate system is chosen such that $k_1 > k_2 > k_3$ (see Eq. 66). The methyl moiety is in the $+x$, $+y$ and $+z$ octant resulting, by Eq. 66, in a positive perturbing potential and a positive rotational strength for the $n - \pi^*$ transition. From Ref. 26.

Tinoco [28], that they were both correct but were each relevant to different electronic transitions. The polarizability theory applied to electronic transitions with strong electric transition dipole moments but little or no inherent magnetic transition dipole moment whereas the Eyring one electron theory applied to electronic transitions with strong magnetic transition dipole moments but with weak electric transition dipole moments, e.g., for transitions with extinction coefficients of less than 1000. It should be noted that Jones and Eyring [29] had already extended the one electron theory to a many electron theory in 1961 prior to the resolution of the controversy so well put forward by Tinoco [28] in 1964. This is one of many contributions that Eyring made in the area of quantum mechanics. Of course, the text *Quantum Chemistry* by Eyring, Walter and Kimball is one of the most commonly used texts in quantum mechanics, having gone through over twenty printings and having been translated into many languages.

7. EYRING'S STATURE AS A 20th CENTURY PHYSICAL CHEMIST

In this sketch, an effort has been made to picture the lecturer and to include some of the equations and derivations that were such an integral part of his models of research. Volumes could be written in this vein but all would seem homely in comparison to the subject and his own expositions. Additional volumes could be written about the person of this dynamic, kindly, and charismatic human being. Much relevant information, both personal and professional, has been compiled in the history thesis of S. H. Heath [31]. Remaining with the scientific perspective, perhaps one of the more elegant statements about this 20th century physical chemist was due to Hugh Taylor in the event of the Eyrings' move from Princeton to Utah. Taylor said of Eyring, "One might say that he possesses the Midas touch. Everything in scientific research turns to gold when brought to the attention of his fertile brain." This was said after Taylor referred to Eyring as "one of the outstanding theoretical chemists of this age, perhaps any age." Eyring was only in his early forties at the time.

So significant has been his work, so great its impact, and so extensive his list of honors and prizes that any relevant award that lists Henry Eyring as a recipient is inevitably enhanced by this demonstration of judgment.

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